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# CERAMIC PIGMENTS WITH DIOPSIDE AND ANORTHITE STRUCTURES BASED ON WOLLASTONITE

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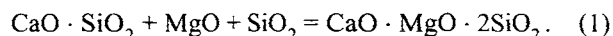
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Ceramic pigments with the structures of diopside and anorthite are obtained from natural wollastonite. It is demonstrated that the reactions of synthesis of diopside structure occur in several stages with formation of intermediate products. Mineralizing additives are required for a more complete phase formation of the anorthite structure. The obtained pigments have a vivid color and can be used to decorate porcelain, faience, and majolica products.

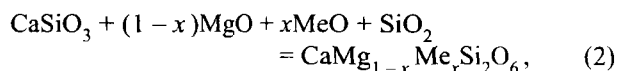
Ceramic pigments based on natural calcium and magnesium silicate (with the structures of diopside, wollastonite, magnesium metasilicate, and forsterite) were obtained and described in a number of studies [1–4]. Pigments of wollastonite composition were successfully used in overglaze paints and glazes.

For fuller use of natural raw resources and to enlarge the color range of ceramic pigments, it is expedient to use natural wollastonite material to synthesize pigments with different crystal structures containing calcium and silicon oxides.

Thus, for example, the diopside chain structure differs from the wollastonite chain only by the spatial arrangement of  $[\text{SiO}_4]^{4-}$  tetrahedrons. Moreover, the presence of  $\text{Mg}^{2+}$  in the composition of diopside  $\text{CaO} \cdot 2\text{SiO}_2$  provides for more intense incorporation of pigment ions in its lattice, since the sizes of the pigment ions are close to the ionic radii of  $\text{Mg}^{2+}$ . The synthesis of a diopside structure based on wollastonite can be accomplished according to the following reaction:



Synthesis with chromophores was performed according to the reaction:



where  $x = 0.1 - 1.0$  mole.

The material used in the study was concentrated Slyudyanskoe wollastonite with a 96% content of the main mineral and not more than 0.1% pigment impurities. Finely milled wollastonite with magnesium oxide and silicon diox-

ide additives was treated with salt solutions of 3d-subgroup transition elements. Firing was performed at the temperature of 1100–1300°C. The composition of the pigment mixtures is given in Table 1.

The pigments were applied as underglaze paints to majolica products. The results of visual inspection of the pigments and paints are presented in Table 2.

It should be noted that as the chromophore content in the pigment composition increases from 0.1 to 1.0 mole, their color varies, which makes it possible to obtain different shades of the same color.

X-ray phase analysis showed that the synthesis reactions proceed in several stages. In the first stage, the additive components produce forsterite and a small quantity of magnesium metasilicate, and later diopside appears. The reaction products are represented by a solid solution which contains diopside as the main phase ( $d = 3.34, 2.99, 2.99 \text{ \AA}$ ), as well

TABLE 1

Pigment	Quantity of MeO moles	Mass content, %					
		CaSiO <sub>3</sub>	MgO	SiO <sub>2</sub>	CoO	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
P-1	0.1	52.80	16.48	27.31	3.41	—	—
P-2	0.5	49.67	8.62	25.69	16.02	—	—
P-3	1.0	46.25	—	23.92	29.83	—	—
P-4	0.1	51.01	15.93	26.39	—	6.67	—
P-5	0.5	42.65	7.40	22.05	—	27.90	—
P-6	1.0	35.39	—	18.31	—	46.30	—
P-7	0.1	50.84	15.87	26.30	—	—	6.99
P-8	0.5	42.05	7.29	21.76	—	—	28.90
P-9	1.0	34.58	—	17.89	—	—	47.53
KhP	—	53.64	18.61	27.75	—	—	—

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TABLE 2

Pigment	Pigment color, firing temperature 1200°C	Underglaze paint color, firing temperature 1050°C
R-1	Light lilac	Light lilac
R-2	Pinkish-lilac	Bluish-violet
R-3	Lilac	The same
R-4	Grayish-light blue	Grayish-green
R-5	Green	Green
R-6	Grass green	Grass green
R-7	Cream	Yellowish-brown
R-8	Brown	Brown
R-9	Chocolate brown	Chocolate brown

TABLE 3

Pig- ment	Quantity of MeO moles	Mass content, %					
		CaSiO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CoO	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
A-1	0.1	42.16	33.31	21.81	2.72	—	—
A-2	0.5	43.89	19.26	22.70	14.15	—	—
A-3	1.0	46.25	—	23.92	29.83	—	—
A-4	0.1	41.02	32.40	21.21	—	5.37	—
A-5	0.5	38.31	16.81	19.82	—	25.06	—
A-6	1.0	35.39	—	18.31	—	46.30	—
A-7	0.1	40.91	32.31	21.16	—	—	5.62
A-8	0.5	37.83	16.60	19.57	—	—	26.00
A-9	1.0	34.58	—	17.89	—	—	47.53
KhP	—	41.75	36.65	21.60	—	—	—

TABLE 4

Pigment	Pigment color, firing temperature 1200°C	Underglaze paint color, firing temperature 1050°C
A-1	Cornflower blue	Ultramarine
A-2	Violet blue	Blue
A-3	Violet	Dark blue
A-4	Lettuce green	Grayish-green
A-5	Green	Green
A-6	The same	Grass green
A-7	Light brown	Pinkish-brown
R-8	Brown	Chocolate brown
R-9	Dark brown	The same

as residual wollastonite ( $d = 3.08, 2.88, 2.55 \text{ \AA}$ ), magnesium silicate ( $d = 3.48, 3.20, 2.45 \text{ \AA}$ ), and forsterite ( $d = 3.88, 3.70, 2.25 \text{ \AA}$ ) at the firing temperature of 1200°C (Fig. 1).

Introduction of chromophores instead of magnesium oxide produces cristobalite ( $d = 4.05 \text{ \AA}$ ) or spinels  $\text{MgFe}_2\text{O}_4$  ( $d = 1.48, 1.61 \text{ \AA}$ ) and  $\text{MgCr}_2\text{O}_4$  ( $d = 4.813, 2.945, 2.512 \text{ \AA}$ ),

TABLE 5

Pigment	Color coordinates		Predominant wavelength, nm	Tone purity, %
	x	y		
R-1	0.36	0.26	528	14
R-2	0.37	0.28	507	14
R-4	0.24	0.34	493	34
R-6	0.35	0.46	561	57
R-7	0.39	0.35	595	25
R-9	0.55	0.315	617	63
A-1	0.23	0.22	475	20
A-2	0.19	0.20	478	35
A-4	0.33	0.40	555	32
A-5	0.31	0.44	543	44
A-7	0.39	0.42	573	55
A-8	0.42	0.34	605	30

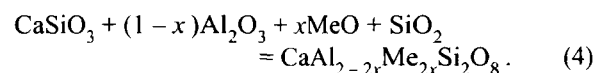
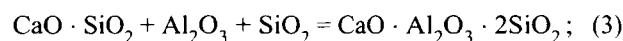
depending on the composition. Cobalt oxide is not identified in any case, and chromium and iron oxides are registered in free form with a content of 0.5 mole (28 wt.% of the pigment mixture).

With small amounts of chromophores, the yield of diopside increases, and their mineralizing effect is observed (Fig. 2). With an increase in the chromophore content, the intensity of the main diopside peak decreases. The pigment ions are not fully assimilated due to their crystalline and chemical distinctions from the replaced ion, they saturate the crystal lattice of the mineral and are released as free oxides at the crystal grain boundaries, thus impeding phase formation of the main mineral.

The pigments with diopside structure based on wollastonite have attractive color, are resistant to high temperatures and melted glaze. They can be used to produce underglaze and overglaze paints and to color glazes.

Another mineral which is anorthite  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  belongs to feldspars. It has a skeleton structure consisting of  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedrons. The spaces between the tetrahedrons are filled with  $\text{Ca}^{2+}$  cations. This structure of anorthite makes it possible to obtain a continuous series of solid solutions.

The synthesis of pigments with an anorthite structure based on wollastonite was performed according to the following reactions:



The generalized designation of MeO denotes oxides of both divalent and trivalent metals. The perturbation of the electric charge balance was compensated by introduction of NaF mineralizer or the formation of defects in the crystal

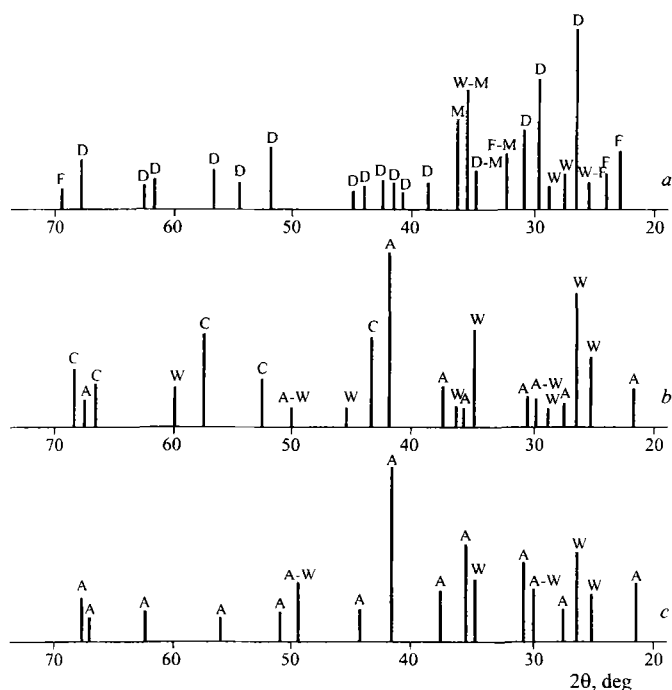


Fig. 1. X-ray diffraction pattern of blank samples at the firing temperature of 1200°C: a) reaction (1); b) reaction (3); c) reaction (3) with a mineralizer; D) diopside; F) Forsterite; M) magnesium metasilicate; C) corundum; A) anorthite, W) wollastonite.

structure. The chromophores in this case were represented by iron, chromium, and cobalt oxides which were added in the form of salt solutions to the crushed mineral with additives of aluminum and silicon oxides (depending on the composition). The chemical composition of the pigments is shown in Table 3.

Table 4 represents the data from visual observation of the pigments and paints with an anorthite structure. Even with a low concentration of chromophores, the pigments exhibit a deep color and are resistant to the dissolving action of the glaze.

X-ray analysis revealed that as a consequence of the reaction of synthesis of the anorthite structure based on wollastonite, a solid solution of complex composition is formed which contains anorthite ( $d = 4.07, 3.20, 2.135 \text{ \AA}$ ), wollastonite ( $d = 3.08, 2.88, 2.55, 1.98 \text{ \AA}$ ), and corundum ( $d = 2.08, 1.838, 1.599 \text{ \AA}$ ).

As the firing temperature increases to 1300°C and  $\text{H}_3\text{BO}_3$  mineralizer is added, the yield of anorthite increases

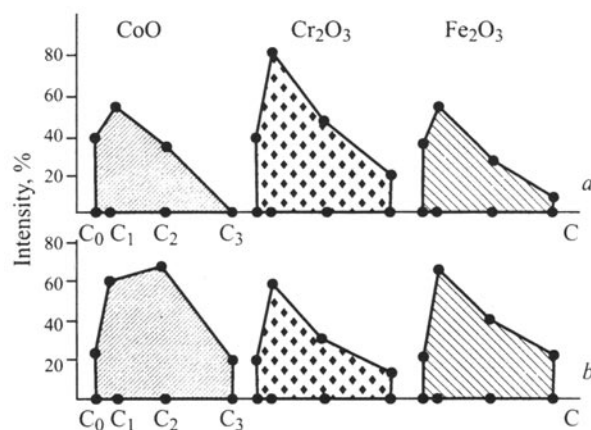


Fig. 2. Variation in the relative intensity of diopside ( $d = 2.99 \text{ \AA}$ ) and anorthite ( $d = 3.20 \text{ \AA}$ ) peaks versus the chromophore concentration in pigments (firing temperature 1200°C): a) reactions (1) and (2); b) reactions (3) and (4);  $C_0, C_1, C_2, C_3$  are 0, 0.1, 0.5 and 1.0 mole respectively.

(Fig. 1). Small amounts of chromophore also have a mineralizing effect and contribute to an increase in anorthite formation (Fig. 2). With an increase in the content of the coloring oxides in the pigment composition, the intensity of the anorthite peaks decreases. Iron and chromium oxides are manifested in free form when their content is about 16%. The spinel  $\text{CoAl}_2\text{O}_4$  ( $d = 2.86, 2.44, 1.56, 1.43 \text{ \AA}$ ) is identified in cobalt pigments.

The color characteristics of the pigments obtained are shown in Table 5.

Thus, using additives and combinations of various components it is possible to obtain ceramic pigments with the structure of diopside and anorthite based on wollastonite. This makes it possible to expand the color range of ceramic pigments and to extend the use of the mineral materials.

## REFERENCES

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